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## DYNAMICS OF PHASE TRANSITIONS

# Calculation of the Nucleation Barrier and Interfacial Free Energy of New-Phase Nuclei by the Thermodynamic Integration Method Using Molecular Dynamics Simulation Data

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**Abstract**—An approach to determining the nucleation barrier and interfacial free energy (surface tension) based on molecular dynamics simulations of structural transformations, in particular, the formation of new phase nuclei, is reported. The approach is based on the thermodynamic integration method, wherein key elements are trajectories characterizing the potential energy change, which are obtained from independent numerical experiments. An important feature of the approach is its applicability to both equilibrium and nonequilibrium systems, as well as the possibility of determining the above thermodynamic characteristics for small new-phase nuclei, with a significant curvature of the surface. For example, we present the temperature dependencies of the surface tension of water droplet nuclei for water vapor nucleation and of the nucleation barrier to crystal nucleation in two model glassy systems, which are computed within the framework of the proposed approach. The calculated values of the surface tension coefficient of water droplet nuclei are compared with the available experimental data.

*Keywords*: thermodynamic integration, molecular dynamics, nucleation barrier, free energy, surface tension
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## INTRODUCTION

With the development of methods for numerical modeling of equilibrium and nonequilibrium processes in many-particle systems, problems associated with interpreting simulation results and finding various physical parameters of such systems have become topical [1–6]. The specificity of simulations in *classical molecular dynamics*, associated with the possibility of obtaining information on the trajectories and velocities of the molecules (atoms) of the system, naturally ensured a fairly successful application of this simulation method to finding pair and many-particle distribution functions, temporal correlation functions, and spectral densities of correlation functions, which made it possible to compare simulation results with experimental data, in particular, in dielectric, neutron, and X-ray spectroscopies [7, 8]. Nevertheless, various thermodynamic parameters, such as free energy and configurational entropy are mostly calculated by techniques based on the Monte Carlo method [9], in which the characterization and statistical treatment of possible structural configurations of the system under specified external conditions are carried out fairly accurately. For example, the Monte Carlo simulation for replica exchange Markov chain [10] and umbrella sampling method, in which the Monte Carlo method is adapted to computation of the free energy as a function of a reaction coordinate, an order parameter, which allows one to determine the so-called energy landscape of the system [11, 12]. The difficulties in calculating the free energy by the Monte Carlo method arise for a system with strongly nonequilibrium effects [13].

Attempts to adapt simulations of molecular dynamics directly to solution of problems associated with determination of the free energy led to the emergence of a number of methods, notably metadynamics simulations, proposed and developed by M. Parinello's group [14, 15], and the thermodynamic integration method [16]. In the present work, we demonstrate that the thermodynamic integration method can be applied to calculating various thermodynamic parameters, such as the nucleation barrier and the interfacial free energy of the critically-sized nucleus of a new phase. Section 1 describes the thermodynamic integration method as applied to calculating the absolute values of the free energy. Sections 2 and 3 demonstrate how this method is applied to determining the nucleation barrier and interfacial free energy, respectively. Lastly, the results of molecular dynamics calculations of condensation of the water droplets and the